Uptake and Release of Cesium-137 by Five Plant Species as Influenced by Soil Amendments in Field Experiments

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ABSTRACT

Phytoextraction field experiments were conducted on soil contaminated with 0.39 to 8.7 Bq/g of ^{137}Cs to determine the capacity of five plant species to accumulate ^{137}Cs and the effects of three soil treatments on uptake. The plants tested were redroot pigweed (*Amaranthus retroflexus* L. var. *aureus*); a mixture of redroot pigweed and spreading pigweed (*A. graecizans* L.); purple amaranth (*A. cruteus* L.) × Powell's amaranth (*A. powellii* S. Watson), referred to here as the amaranth hybrid; Indian mustard [*Brassica juncea* (L.) Czern.]; and cabbage (*Brassica oleracea* L. var. *capitata*). For control plants, the concentration ratios (CR) of ^{137}Cs were greatest for redroot pigweed and the amaranth hybrid, with average CR values of 1.0 ± 0.24 and 0.95 ± 0.14, respectively. The lowest value was for Indian mustard at 0.36 ± 0.10. The soil treatments included (i) application of NH_4NO_3 solution to the soil after plants had matured, (ii) addition of composted manure to increase organic matter content of the soil, (iii) combination of the manure and ammonium solution treatments, and (iv) controls. The ammonium solution gave little overall increase in accumulation of ^{137}Cs. The use of composted manure also had little influence, but the combination of the composted manure with application of ammonium solutions had a distinctly negative effect on plant uptake of ^{137}Cs. On average the fraction of ^{137}Cs taken up from the soil was reduced by 57.4 ± 1.2% compared with controls. This was the result of release of competing ions, primarily Ca, from the manure and was observed across all five plant species tested. The application of ammonium solution took place in the last two weeks before harvest. The reduction of plant ^{137}Cs content, by addition of the ammonium solution, as it interacted with the manure, indicates that substantial quantities ^{137}Cs can be released from the shoots of plants as a result of sudden changes in soil solution chemistry.

Contamination of soil with ^{137}Cs is a significant problem at many nuclear installations. Current remediation practices are costly and include excavation, shipping, and burial of contaminated soil at licensed radioactive waste disposal facilities. This has created the need for a way to effectively and selectively remove ^{137}Cs from the soil. One possible technique is phytoextraction, a process that uses plants to accumulate contaminants in their aboveground tissue. Once the plants are harvested, volume reduction techniques (e.g., low-temperature ashing) can be applied to the biomass resulting in an estimated 100-fold reduction in the quantity of contaminated solids requiring disposal. Given sufficient uptake of ^{137}Cs into the plants and sufficient annual biomass production in fields (this often presents significant agronomic problems), this approach could provide an economically advantageous system for decontaminating soils containing ^{137}Cs. This is especially true at sites where there are no disposal facilities for radioactive waste and shipping large volumes of contaminated soil to a distant radioactive waste disposal facility is costly.

In the early 1960s soil contaminated with ^{137}Cs was inadvertently used as fill ("landscaping soil") at several locations around Brookhaven National Laboratory and has become the subject of a set of experiments to investigate phytoextraction of ^{137}Cs. This radionuclide, a fission product with a half-life of 30 yr, presents especially difficult issues for phytoextraction. As a carrier-free tracer, ^{137}Cs tends to have relatively high K_D values (the soil–water partition coefficient, where K_D = ^{137}Cs concentration in soil/^{137}Cs concentration in water) with most soils, meaning that it tends to be relatively immobile (Sheppard and Thibault, 1990; Baes et al., 1984). While the high K_D means that the ^{137}Cs remains accessible at the surface, it also means that it tends to stay bound to the soil and is difficult to extract. This is especially so in soils containing mica and illite minerals, which preferentially incorporate Cs into interlattice positions (Tamura and Jacobs, 1960). To exacerbate the difficulty of phytoextraction of ^{137}Cs, Cs is a K analog. Plants require significant concentrations of bioavailable K, so addition of K in fertilizer is often required at remediation sites to increase biomass production. However, addition of this nutrient will dilute uptake of Cs, which is present in much lower molar quantities (by many orders of magnitude) than K. In hydroponic studies, plant roots preferentially take up K over Cs, but this selectivity seems to be dependant on concentration (Zhu and Smolders, 2000 and references therein). This effect is less clear when Cs is associated with soil, but addition of K to soil has been shown to reduce uptake of Cs by plants (Robison and Stone, 1992). Models of plant uptake of ^{137}Cs often include terms for soil concentrations of elements that compete with Cs for uptake, such as available K and ammonium.

Solutions containing K or ammonium salts can elute Cs from soil to a limited extent and, although they may compete with Cs for uptake by plants, they have been shown to increase accumulation of ^{137}Cs. Dushenkov et al. (1999), in experiments with soil contaminated by the Chernobyl accident, determined that ammonium sulfate provided optimal elution of Cs from soil but no statistically significant increase in uptake by *Amaranthus* spp. Lasat et al. (1997) showed that with cabbage, addition of 40 and 80 mmol of NH_4NO_3 per kg of soil from Brookhaven National Laboratory (in pot experiments)

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Abbreviations: CR, concentration ratio.

increased uptake of ^{137}Cs to CR values of 1.8 and 2.8 respectively, from the CR value of 1.0 for the controls. In earlier studies on the landscaping soil (Table 1), about 10% of the ^{137}Cs was mobilized to the aqueous phase by a variety of solutions (Fuhrmann et al., 1996). Ammonium and K salts were mildly effective, eluting about 10% of the ^{137}Cs, while strong acids eluted about 34%. Use of strong chelating agents to elute ^{137}Cs from the soil to make it available for uptake by plants is not useful because Cs tends to form only very weak complexes.

Soils with large proportions of organic matter tend to allow greater plant accumulation of Cs. Sanchez et al. (1999) examined uptake by bentgrass (*Agrostis capillaris* L.) of ^{134}Cs from natural soils that contained from 12.6 to 96.5% organic matter. Concentration ratios were positively and significantly correlated to organic matter, which in turn allowed greater availability of Cs to the soil solution due to the low clay content, low concentrations of available K, and high ammonium concentrations.

The purpose of the work reported here was to extend earlier greenhouse and field studies to determine the potential of phytoextraction to meet the cleanup goal of 0.85 Bq/g for ^{137}Cs at the landscaping soil sites. We have estimated that at least 40 crops would be required to extract sufficient ^{137}Cs from the soil to meet cleanup requirements, based on data from an earlier field study using redroot pigweed (Lasat et al., 1998). Although the accumulation of ^{137}Cs in this species was exceptional, with concentration ratios (CR) averaging 2.58 and plant concentrations of 67 kBq/m^2, the time required would be too great. Consequently, any approach to providing more rapid removal would be beneficial. The experiments discussed in this paper explore several approaches to enhancing plant uptake of ^{137}Cs from soils containing low concentrations of this radionuclide. The specific objectives of the work were to (i) assess the ability of several species, including three species of *Amaranthus*, to accumulate ^{137}Cs; (ii) examine the effect of several soil amendments and treatments on uptake of ^{137}Cs by the selected plant species; and (iii) provide field information on biomass and plant uptake at a specific contaminated site where ^{137}Cs is confined to the top 15 cm of the soil.

Table 1. Quantity of ^{137}Cs eluted from the landscaping soil (Fuhrmann et al., 1996).†

Reagent	Molarity	^{137}Cs in liquid
		%
Acetic acid	1	0.5, 0.7
Citric acid	1	1.5, 3.2
EDTA	saturated	3.0, 4.5
CsCl	1	5.3, 7.6
NH_4F	1	11.0, 10.1
H_2O_2	30%	2.0, 2.7
NH_4Cl	0.5	9.7
NH_4Cl	1	9.7
NH_4Cl	2	9.9, 10.8
KCl	1	8.5
KCl	2	6.2
HCl + HNO_3	concentrated	37.6, 30.4

† The conditions of these tests were 4 g of soil and 12 g of solution with a 3-h contact time. The liquid was filtered through 0.45-μm filters. In some cases a second soil sample was tested and the results also are shown.

MATERIALS AND METHODS

Soil

The study was conducted on a field plot established on the contaminated landscaping soil. The plot measured approximately 4 × 20 m and contained 88 randomized experimental cells, each measuring 0.5 m on a side. Eighteen soil locations were sampled for radionuclides before planting. These data were mapped with Surfer (Golden Software, 2003) and concentrations of ^{137}Cs were estimated from the contours. The ^{137}Cs activity at this site ranged from 0.39 to 8.7 Bq/g. The contamination was generally confined to the upper 15 cm of the soil. The soil at Brookhaven National Laboratory is a coarse-loamy, mixed, mesic Typic Dystrochrept. It is generally well drained and formed as a mantle of sandy loam over thick deposits of sand and gravel. Mineralogy is dominated by quartz with percentages typically around 90% or more. Rock fragments range from 2 to 23% with higher percentages in gravel fractions. Micaceous minerals represent no more than a few percent. Iron coatings are common in the top 1 m. Additional soil parameters are given in Table 2. Soil fertility, as indicated by P, K, and N levels, was extremely low.

The soil was first treated with Roundup (Scotts Company, Marysville, OH), a glyphosate (*N*-phosphomethylglycine) herbicide. The test area was then repeatedly plowed with a tractor equipped with a rotary plow. Air samples taken downwind and adjacent to the site during all work that could induce airborne contaminants (plowing and harvesting) showed no airborne radioactive material. Before planting, each cell received 60 g/m^2 of crushed limestone and 40 g/m^2 of commercial P–K–N fertilizer. The experimental matrix for the field study used a factorial design with two parameters: plant species and soil treatments.

Plants

The plant species were redroot pigweed, a mixture of redroot pigweed and spreading pigweed, the amaranth hybrid, Indian mustard, and cabbage. In earlier work we observed that redroot pigweed provided especially good uptake of ^{137}Cs (Fuhrmann et al., 2002). The various *Amaranthus* species were used to determine if there is similar uptake of ^{137}Cs by different species of this genus. The combination of redroot pigweed and spreading pigweed was inadvertent as the seed mixture received from the supplier was a mix rather than redroot pigweed alone. Indian mustard is a species frequently used in phytoremediation of metals (Blaylock et al., 1997) and served as a reference. Previous experiments indicated that cabbage was able to accumulate significant quantities of ^{137}Cs in greenhouse experiments, especially when the soil was treated with

Table 2. Soil characteristics for the landscaping soil.

Parameter	Sample 1	Sample 2
CEC†, $cmol_c$/kg	15.6	11.5
Alkalinity, mg/L	30.0	32.2
Chloride, mg/L‡	16.6	13.3
Electrical conductivity, μS/m‡	221	185
Nitrate + nitrite N, mg/L‡	3.9	5.0
Orthophosphate, mg/L‡	0.85	1.36
K, mg/L‡	3.5	3.5
Sulfate, mg/L‡	53	56
Total organic C, %	1.62	1.80
pH‡	5.80	5.92
Sand, %	75	75
Silt, %	22	22
Clay, %	2	2

† Cation exchange capacity.
‡ Results from a 1:1 water extraction.

an ammonium nitrate solution (Lasat et al., 1997). In this experiment we extended this approach to a field setting.

All plants were started in the greenhouse in potting soil mix. Plants were watered as needed with a basic nutrient solution. After two to three weeks of growth, they were transplanted into the field cells, six to nine plants per cell for a total of more than 600 plants. They were transplanted in late summer and grown for two months. The site was enclosed by a high fence to exclude wildlife. The field was watered by spray irrigation, as needed. To minimize weed growth and the spread of contaminated soil the areas between the cells were covered with straw.

Soil Treatments

Soil treatments were designed to determine if enhanced accumulation of ^{137}Cs in plants could be attained by (i) amending contaminated soil with organic matter, (ii) applying ammonium nitrate solution to the soil before harvest, or (iii) a combination of the two. These treatments were selected because earlier work showed that ammonium could provide enhanced uptake of ^{137}Cs from this soil in pot studies (Lasat et al., 1997). In addition, as discussed earlier, there is a positive relationship between organic matter content of soils and plant uptake of ^{137}Cs. There was the possibility that addition of organic matter to the soil, after contamination occurred, might also provide enhanced uptake.

For each species there were four sets of experimental cells, with each set receiving one of the treatments listed below. There were three to seven replicate cells for each. The treatments included (i) application of NH_4NO_3 to the soil after plants had matured (2 L per cell of 0.1 *M* solution three times in the two weeks before harvest); (ii) addition of composted manure to field soil when the plants were transplanted (0.5 kg/cell); (iii) combination of manure and NH_4NO_3 solution treatments; and (iv) controls (no manure, water was applied instead of NH_4NO_3 solution). The manure amendment was Agway (Binghamton, NY) composted manure and organic humus. This material was labeled as containing 0.5% soluble K_2O.

Analysis

At harvest, plants were cut a few centimeters above the soil, rinsed in clean tap water, and placed in large preweighed paper bags. Total fresh weight of plants from each cell was measured. Plants were dried at 60°C for several days and the dry weight was determined. A survey of ^{137}Cs activity in each sample was made by placing the bagged sample over an intrinsic germanium γ-ray detector for 2 min. High-activity samples were then analyzed in a bag monitor (Canberra Industries, Meriden, CT) that contained six detectors and was calibrated to ^{137}Cs. Lower activity samples were analyzed on planar, intrinsic germanium γ-ray spectrometers using a Canberra data analysis system. These samples were formed into a standard geometry by pressing them (at 450 kg maximum) into plastic containers (19 cm in diameter) using a hydraulic press. They were counted on the germanium spectrometers for periods of time ranging from 30 to 1000 min depending on their activity. Each sample was counted twice. First, the sample was counted in the container as it had been pressed. The second time, the sample was removed from the container, turned upside-down, pressed back into the container, and recounted. This was necessary because of the different thicknesses of the samples after being pressed. The average of the two measurements was used. Activity of ^{137}Cs in Bq/g (dry wt.) was then calculated from counts observed under the 661 keV peak. Soil samples were analyzed on the same planar detectors using 20-g (dry wt.) samples in a standard geometry. All detectors were intercalibrated by counting a set of samples on each. A vegetation standard (VEBN from the Environmental Monitoring Laboratory in New York, NY) was used as a secondary standard. For soils, a sediment standard was used from the National Institute of Standards and Technology (Gaithersburg, MD; Standard Reference Material 4350B). Concentration ratios (CR) were calculated as ^{137}Cs concentration in plant/^{137}Cs concentration in soil.

RESULTS

Biomass Production

As shown in Table 3, production of the control cells, as dry weight, was close to 1000 g/m^2 for the redroot pigweed/spreading pigweed mixture, cabbage, and Indian mustard. The lowest production was for the amaranth hybrid, which was just over 500 g/m^2. Plants appeared healthy, with the *Amaranthus* species reaching a height of about 1 m and producing large seedheads. The biomass produced was acceptable, remembering that a balance was being drawn between the quantity of K needed for good growth and the amount that would interfere with ^{137}Cs uptake.

Figure 1 summarizes the effects of the various treatments on biomass production. Biomass of redroot pigweed and the amaranth hybrid showed little change across the four treatments. The same was true for the redroot pigweed/spreading pigweed mixture, with the exception of the manure treatment with which average production increased to 1374 g/m^2. The NH_4NO_3 treatment reduced production of both Indian mustard and cabbage by about 30% relative to the controls. This effect was less pronounced in plants that received both the manure and ammonium treatments.

Concentration Ratios of Cesium-137

For the control plants, the concentration ratio of ^{137}Cs was greatest for redroot pigweed and the amaranth hybrid, with average CR values of 1.0 ± 0.24 and 0.95 ±

Table 3. Data for the control cells.

Species	Concentration ratio†	Production	^{137}Cs removed from soil†	Number of cells
		g/m^2, dry wt.	%	
Redroot pigweed	1.0 ± 0.24	865	0.47 ± 0.15	6
Redroot pigweed/spreading pigweed mixture	0.63 ± 0.24	976	0.40 ± 0.24	5
Amaranth hybrid	0.95 ± 0.14	564	0.31 ± 0.10	6
Indian mustard	0.36 ± 0.10	964	0.18 ± 0.08	4
Cabbage	0.63 ± 0.19	981	0.31 ± 0.09	7

† Values and the 90% confidence intervals.

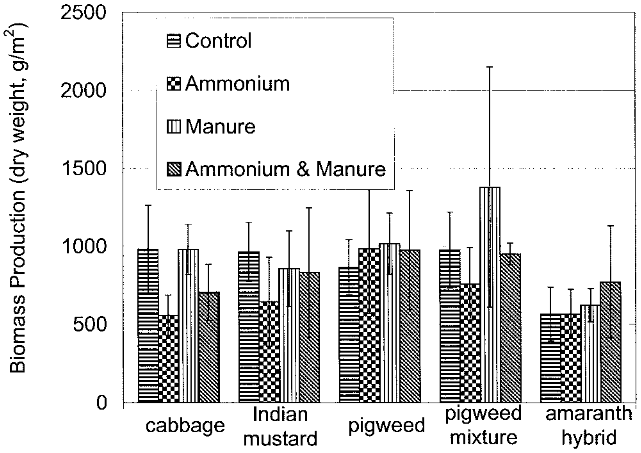

Fig. 1. Biomass production (average values and 90% confidence intervals) of the plant species as influenced by the various treatments.

0.14, respectively. The lowest value was for Indian mustard at 0.36 ± 0.10 (Table 3).

Figure 2 shows that the only combination of species and treatment that indicated improved uptake as measured by the CR was for cabbage with the ammonium solution. In this case the CR averaged 1.19 ± 0.34 (n = 6 cells), higher than the controls, which averaged 0.63 ± 0.19. A t test confirmed that for this species the average CR for the ammonium treatments was different than the controls at the 0.05 probability level. In no other case was uptake increased significantly over that of the controls.

Concentration ratios for Indian mustard were the lowest of the plant species tested, independent of the treatment. Concentration ratios for Indian mustard from the control cells and those receiving ammonium solution were identical while averages of the cells containing manure were slightly lower.

The combination of manure and ammonium solution consistently resulted in CR values lower than the controls, with redroot pigweed and the amaranth hybrid being lower by a factor of two or three. The ammonium solution alone did not result in any CR values that were significantly lower than those of the controls. Manure amendment to the soil, in most cases, resulted in lowered

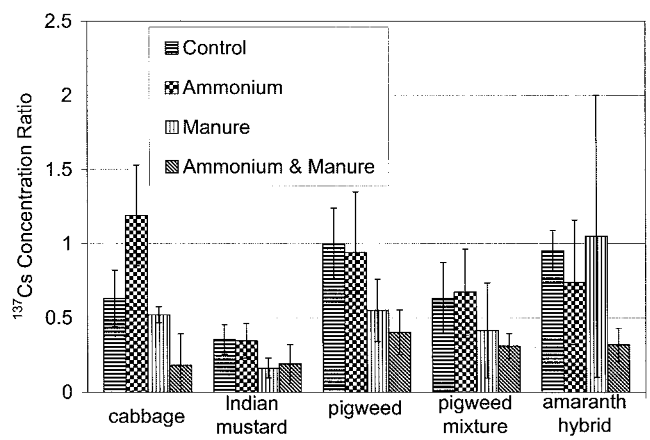

Fig. 2. Concentration ratios (average values and 90% confidence intervals) of the plant species as influenced by the various treatments.

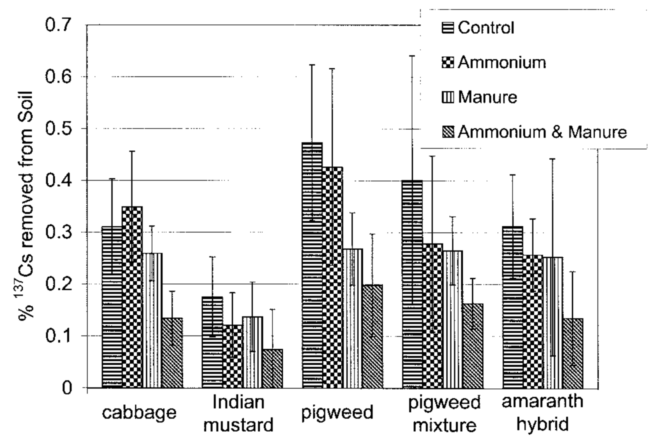

Fig. 3. Percentages of ^{137}Cs removed from the soil (average values and 90% confidence intervals) by the plant species as influenced by the various treatments.

average uptake relative to controls. In the cases of the three *Amaranthus* species, scatter in CR values was very large when the ammonium or manure amendments were applied, making comparisons impossible. But, again, the combination of the two treatments, manure plus ammonium solution, consistently resulted in reduced average uptake of ^{137}Cs. This was true even in the case of cabbage in which the ammonium solution alone increased CR values.

Mass of Cesium-137 Removed from the Soil

While the concentration ratio allows comparison of uptake normalized to concentrations in the soil, the total uptake on a mass (or radioactivity) basis is more relevant for phytoextraction. The total activity accumulated in plant matter for each cell was determined by multiplying the concentration of ^{137}Cs in the plant matter from each cell by the dry biomass produced in that cell. From this the percentage of activity accumulated by the plants, with respect to the total activity in the soil of the cell, was calculated by dividing the total quantity of ^{137}Cs in plants in each cell by the estimated quantity of ^{137}Cs in the soil. The depth distribution of ^{137}Cs was assumed to be homogeneous to 0.15 m and the bulk density was 1200 kg/m^3.

Figure 3 shows the percentage of ^{137}Cs removed from soil by each species and treatment, presenting a slightly different view than the CR values shown in Fig. 2. The data sets each consist of three to seven experimental cells. The wide scatter in uptake relative to concentrations of ^{137}Cs in the soil is the result of relatively small quantities of ^{137}Cs accumulated by the plants from a large mass of soil in each cell. Because of the shallow depth of contaminant distribution, it is likely that plant roots grew into the underlying, uncontaminated soils in some locations, resulting in lower uptake of ^{137}Cs relative to the estimated quantity in the soil. Although this scatter makes interpretation difficult, some useful points can be made. Average percent extraction of ^{137}Cs was greatest for redroot pigweed and the redroot pigweed/spreading pigweed mixture. Indian mustard took up less ^{137}Cs than did redroot pigweed, based on both the CR and the total uptake data. On the basis of the total uptake data alone, because of the large confidence intervals, it is unclear if the other *Amaranthus* species actually performed better than Indian mustard or than each other.

DISCUSSION

Overall, the plants tested removed between 0.08 and 0.47% of the ^{137}Cs contained in the soil. Concentration ratios ranged from 0.1 to 1.2. To put the results from these experiments into context, uptake of ^{137}Cs by various *Amaranthus* species and by cabbage consistently was greater than has been reported for most other species. For most species, typical values for ^{137}Cs range between 0.02 and 0.1 (Wang et al., 1993; Ng et al., 1982; Napier et al., 1988; Baes et al., 1984; Kennedy and Strange, 1992). The CR values of native plants growing on the contaminated soil ranged from 0.02 to 0.13. These plants have very low biomass and we have found that none accumulate significant quantities of ^{137}Cs. Several unidentified grasses growing in the experiment fields had CR values averaging 0.05, three samples of peppergrass (*Lepidium virginicum* L.) had an average CR value of 0.04, and five samples of sheep sorrel (*Rumex acetosella* L.) had an average CR of 0.1.

At least 25 plant species have been tested on the landscaping soil for their ability to accumulate ^{137}Cs. In an earlier field study at Brookhaven National Laboratory, the highest CR values were obtained for redroot pigweed, which ranged from 2.2 to 3.2, while for Indian mustard and tepary bean (*Phaseolus acutifolius* A. Gray) they were 0.4 to 0.5 and 0.2 to 0.3, respectively (Lasat et al., 1998). In the same field marigolds (*Tagetes* spp.) had CR values that ranged from 2.0 to 3.0. In a related field study of 18 cultivars of crop plants grown on the same site, white mustard (*Sinapis alba* L.) and cabbage accumulated the greatest concentrations of ^{137}Cs (Dushenkov et al., 1998). Concentration ratios were not reported for this work and *Amaranthus* species were not included in this set. Dushenkov et al. (1999) reported CR values for a number of *Amaranthus* species that ranged from 0.53 to 2.03 at a site near Chernobyl. In fact the same variety of redroot pigweed was used in both studies and in both cases gave the highest concentrations of ^{137}Cs in shoots as well as biomass yield. The *Amaranthus* species, given their relatively high biomass production and the elevated CR values that have been reported, have potential for ^{137}Cs extraction. Moreover, they also hold promise for accumulation of ^{90}Sr (Fuhrmann et al., 2002).

Effect of Treatment with Ammonium Solution

For the *Amaranthus* species and Indian mustard, the ammonium treatment provided no increase in CR value or in the average percentage of ^{137}Cs extracted from the soil compared with the controls. While the CR values for cabbage with the ammonium solution were greater than the control or the manure-amended soil, this was no longer the case when considering percent uptake. In fact for this species the control, ammonium, and manure treatments were essentially equal with respect to percent extraction. The ammonium treatment reduced biomass by about 30%, counteracting the higher CR values. Lasat et al. (1997), in pot studies, also noted that the production of shoot biomass was reduced in cabbage receiving ammonium solution treatments. Consequently, growth of this species is inhibited by application of the ammonium solution but the CR values remain higher. While the average percent removal for cabbage was greater with the ammonium treatment than the controls, these differences were not statistically significant. Thus, for all species the ammonium treatment provided no increase in uptake. At Chernobyl, uptake of ^{137}Cs in redroot pigweed (var. *myronivka*) in plants treated by the addition of ammonium nitrate and ammonium sulfate solutions was not statistically different from the controls (Dushenkov et al., 1999).

Effect of Manure Amendment

Addition of manure did not increase extraction of ^{137}Cs. As shown in Fig. 2 and 3, in all species the average CR and percent extracted were lower than the control, but often not beyond the confidence interval. The decrease was not the result of the manure diluting the soil since the manure comprised 0.5 kg out of about 45. Several authors have reported that organic-rich soils result in relatively high uptake of ^{137}Cs by plants (e.g., Sanchez et al., 1999). In those experiments ^{137}Cs was added to soil that naturally contained organic matter, with the ^{137}Cs sorbing directly on organic matter, which typically has a poor capacity to retain it. It was unclear if addition of uncontaminated organic matter, after the soil had sorbed the ^{137}Cs, would also result in improved uptake. Based on our set of experiments, this does not appear to be the case.

Effect of Combined Ammonium and Manure Treatments

In all species the combination of ammonium and manure resulted in reduced average CR values for ^{137}Cs, compared with the controls. Table 4 summarizes the

Table 4. Comparison of concentration ratios (CRs) between plants receiving the manure + ammonium treatment and their controls.

Species	CR for ^{137}Cs, controls†	CR for ^{137}Cs, manure + ammonium†	Difference in CR	Probability level	Conclusion
			%		
Cabbage	0.626, 0.099, (7)	0.373, 0.067, (4)	40.4	0.21	not different
Indian mustard	0.355, 0.016, (4)	0.190, 0.024, (4)	46.5	0.15	not different
Redroot pigweed	0.999, 0.127, (6)	0.403, 0.035, (4)	59.7	0.02	different
Redroot pigweed/spreading pigweed mixture	0.632, 0.108, (5)	0.307, 0.008, (3)	51.4	0.15	not different
Amaranth hybrid	0.952, 0.042, (6)	0.318, 0.021, (5)	66.6	0.003	different

† Values represent mean, variance, (n).

Table 5. Comparison of ^{137}Cs uptake between plants receiving the manure + ammonium treatment and their controls.

Species	Uptake of ^{137}Cs, controls†	Uptake of ^{137}Cs, manure + ammonium†	Difference in uptake	Probability level	Conclusion
	%				
Cabbage	0.31, 0.016, (7)	0.13, 0.004, (4)	−56.8	0.05	different
Indian mustard	0.175, 0.011, (5)	0.077, 0.008, (4)	−56.0	0.18	not different
Redroot pigweed	0.473, 0.052, (6)	0.198, 0.015, (4)	−58.1	0.04	different
Redroot pigweed/spreading pigweed mixture	0.401, 0.108, (5)	0.163, 0.003, (3)	−59.4	0.19	not different
Amaranth hybrid	0.312, 0.016, (4)	0.135, 0.015, (5)	−56.7	0.08	different

† Values represent mean, variance, (*n*).

CR values and their statistics allowing a comparison between the controls and plants receiving the combined manure plus ammonium treatment. In addition Table 4 gives percent differences between average CR values of the controls and the treated cells for each species. In all cases the CR was much less for plants receiving the combined treatment than the controls, ranging between 40 and 67% less. Two-tailed *t* tests (for samples with unequal variances) show that the CR values for both the amaranth hybrid and redroot pigweed were significantly different than their controls at the 0.05 probability level.

For the percent removal data, shown in Table 5, cabbage and redroot pigweed averages indicate that uptake in plants receiving the combination of ammonium solution and manure also was significantly different (at the 0.05 probability level) from the controls. Uptake by the amaranth hybrid was different from its controls at the 0.08 level. Remarkably, the reduction of ^{137}Cs accumulation by all species ranged between 56.0 and 59.4%. In spite of the high variability in these data, a problem often found in real sites (especially those contaminated with fission products), all averages of the combined manure and ammonium treatments are below those of the controls. Moreover, the CR and the percent uptake data sets show that reduction was statistically significant for three of the species. The combination of manure added to the soil and the subsequent addition of ammonium solution resulted in less accumulation of ^{137}Cs in a variety of plant species.

This strongly reduced accumulation of ^{137}Cs may have been caused by release of K and other ions from the manure when the ammonium solution was applied. These elements may have then competed with Cs for plant uptake. To test this contention, an experiment was conducted with some of the same batch of composted manure that was added to the soil. One gram of dry compost was added to 25 g of distilled water, and another gram was added to 25 g of 1 *M* ammonium nitrate solution. After 20 h the mixtures were filtered, brought to a standard volume (50 mL) and analyzed by inductively coupled plasma optical spectroscopy for a variety of metals. The concentrations of eluted elements in water and the ammonium solution are shown in Table 6. Both water and the ammonium solution eluted more Ca than any other element tested. The Ca release was almost twice as high for the ammonium solution as for the water, with a difference of 0.15 mmol/g. In contrast, the difference in K release was small, only about 0.078 mmol/g for water compared with 0.091 for ammonium; a difference of 17% more. Releases of Mg by the ammonium solution were 0.01 mmol/g greater than by water. While it is not known how these concentrations compare with those of pore water in the field, the combined increased release of Ca, Mg, and K due to elution by the ammonium solution probably results in reduced plant concentrations of ^{137}Cs.

The mechanisms by which Cs is taken up by plants and the competition by K and other elements with ^{137}Cs for uptake have recently been reviewed (Zhu and Smolders, 2000; White and Broadley, 2000). Since monovalent cations move through the root by the symplastic pathway (Marschner, 1995), these ions must cross through cell membranes at least twice before entering the xylem. Transport of K^+ proceeds via several processes. When concentrations of K^+ external to the cell are very low, symport proteins are active. At higher external concentrations, K^+ crosses the membrane by diffusion through specific K^+ channels (Taiz and Zeiger, 1998). Transport of Cs^+ across these membranes occurs via several channels with the dominant influx occurring via nonspecific cation (voltage insensitive) channels (White and Broadley, 2000; White et al., 2003). Influx through these channels is partially inhibited by Ca and other multivalent cations. Other influx, through Cs^+ and H^+ symporters, also may take place but at a lower rate (White et al., 2003). Efflux of Cs^+ from the cell to the xylem appears to be controlled by outward rectifying K^+ channels (White et al., 2003).

The divalent cations Ca^{2+} and Mg^{2+} inhibit the uptake of ^{137}Cs, but to a smaller extent than K. For example, in a solution culture experiment using spinach (*Spinacia oleracea* L.), an increase in Ca + Mg concentration by

Table 6. Elution of elements from composted manure.

Element	Eluted by water	Eluted by NH_4NO_3	Element eluted by water in each field cell	Element eluted by NH_4NO_3 in each field cell
	mmol/g of manure		mmol	
Na	0.021	0.019	10.5	9.5
Ba	3×10^{-6}	0.0007	0.0015	0.35
Mg	0.039	0.049	19.5	24.5
K	0.078	0.091	39	45.5
Ca	0.135	0.285	67.5	143
Sr	0.0001	0.0003	0.05	0.15

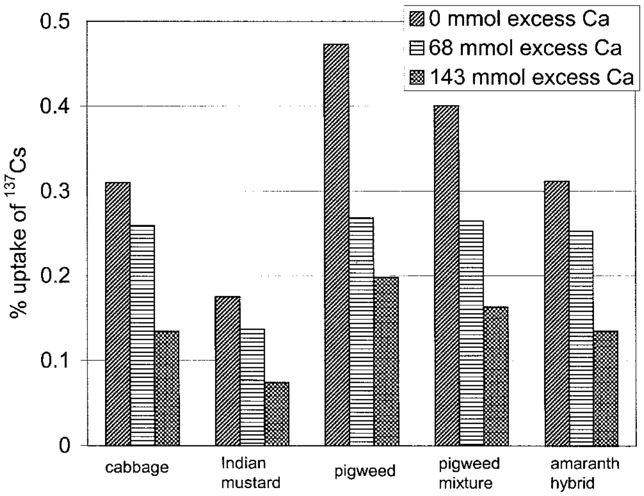

Fig. 4. The concentration of ^{137}Cs taken up by plants as a function of the estimated quantities of Ca released from composted manure by water and ammonium solution in the field cells. Zero excess Ca is defined as Ca released by the soil (and limestone added) in a cell (control cells). Cells containing manure released about 67 mmol of Ca, while cells containing manure and the ammonium solution released about 143 mmol Ca.

a factor of about 26 (from 0.27 to 7.0 mM in the solution) decreased uptake of ^{137}Cs by a factor of 3 (Smolders et al., 1997a). The effect also extends to ^{137}Cs associated with soil. Strebl et al. (2002) found that transfer factors of ^{137}Cs in meadow vegetation were negatively correlated to pH and exchangeable Ca and Mg, as well as total Ca, Na, and Mg. In our experiments, average CR values, shown in Table 4, indicate that this effect was brought about by the use of ammonium solution that eluted significantly more Ca from the manure than did the water. The small differences in releases of K and Na between the water and ammonium solution suggest that these elements were not the cause of this effect. The manure, on application of the ammonium solution, appears to have supplied enough additional ions (primarily Ca^{2+}) to the soil solution to reduce concentration of ^{137}Cs in plants.

For 500 g of manure in each cell, water released about 68 mmol of Ca while the 6 L of the ammonium solution released about 143 mmol. Assuming that the water-removable fraction had already been eluted by rain and irrigation over time, the 6 L of solution applied to the soil would have released about 75 mmol of Ca. The resulting concentration of Ca in the pulse of 6 L could have been as high as 12.5 mM, greater than needed to inhibit uptake of ^{137}Cs as observed by Smolders et al. (1997a, 1997b).

Figure 4 was produced by plotting ^{137}Cs percentage uptake of each plant species (see Fig. 3) as a function of the estimated quantity of excess Ca released in field cells by each treatment as shown in Table 6. This provides a measure of the effect of Ca elution by water and ammonium on uptake of ^{137}Cs. The "excess Ca" values of 0 are the control cells, representing any Ca released by water from the soil and limestone (added to adjust pH) in a cell. The value of 68 mmol is the estimated release of Ca from the 500 g of manure by water, and 143 mmol is the quantity of Ca released from manure by the ammonium solution. Water and the ammonium solution yielded quite similar releases of the other elements; accordingly these elements (e.g., K) are not included in the calculation. Figure 4 shows that excess Ca related consistently to reduced uptake by all of the plant species tested. Release of Ca from soil amendments under field conditions had a deleterious effect on plant concentrations of ^{137}Cs. This effect was greatest for plants that accumulated the most ^{137}Cs.

Since the ammonium solution was applied only in the last two weeks before harvest, it appears that the quantity of Ca eluted from the soil (or amendments) within a week or so of harvest can control the quantity of ^{137}Cs accumulated by plants. The decrease in ^{137}Cs content represents about 50% of the ^{137}Cs in the control plants. It is possible that this effect may be the result of inhibited Cs uptake in response to the high Ca pore fluid in the manure + ammonium cells, compared with continuing uptake in controls. This would mean that the ^{137}Cs content of control plants increased by at least 50% in two weeks; an increase that is highly unlikely. Consequently, the decrease observed in plants from the amended cells must be the result of ^{137}Cs being removed from the shoots within a relatively short time. Buysse et al. (1995) showed that within 12 h, 57% of ^{137}Cs contained in spinach plants was recirculated through the plant and moved through the phloem. Calcium will readily displace ^{137}Cs that is retained in the plant by cation exchange, possibly sorbed on xylem vessels as does Na (Marschner, 1995). Displaced ^{137}Cs may then be translocated to the roots through the phloem, or possibly leached from the leaves as the plant responds to the pulse of Ca taken up. This implies two things. First, a significant fraction of the ^{137}Cs in plants from our experiment is quite mobile and not strongly retained by the shoots. Second, that mobile fraction is sensitive to Ca and about half of the ^{137}Cs contained in the shoots can be released by Ca concentrations on the order of 10 mM in soil fluid. As a result, for phytoextraction of ^{137}Cs, it is essential to minimize applications of soil amendments and/or reagents (or liquid fertilizer) that increase soil solution concentrations of elements that can displace ^{137}Cs, even after a crop is well established and is accumulating the contaminant. The pulse of Ca (and other elements that also may be as effective) cannot only inhibit uptake of ^{137}Cs into the plant, but can remove much of the ^{137}Cs that has accumulated in the shoots, returning it either to the soil or the roots. If a crop is found to have accumulated ^{137}Cs from the soil, it may be possible to significantly reduce concentrations of this radionuclide in plants by applying a Ca solution to the soil a week or two before harvest.

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